



Polymer electrolyte membranes with high selectivity based on silicon-containing sulfonated polystyrene/acrylate, poly(vinyl alcohol) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid)

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HIGHLIGHTS

- The organic/inorganic composite membranes are prepared by blending and crosslinking.
- The composite membranes possess excellent thermal stability and methanol barrier.
- The selectivity of composite membranes is much higher than that of Nafion® 117.
- The composite membranes are particularly promising for DMFC applications.

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ABSTRACT

A series of crosslinked organic/inorganic composite membranes are prepared from silicon-containing sulfonated polystyrene/acrylate, poly(vinyl alcohol) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) by blending and crosslinking. The potential of composite membranes as polymer electrolyte membranes in direct methanol fuel cells (DMFCs) is preliminarily assessed. It is found that these membranes possess excellent thermal stability and methanol barrier. Their methanol diffusion coefficient can be as low as $7.82 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, which is only about 1/30th of that ($2.36 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) of Nafion® 117. In addition, the proton conductivity of the composite membranes is of the order of $10^{-2} \text{ S cm}^{-1}$ and all the membranes show much higher selectivity in comparison with Nafion® 117. The highest selectivity value is $3.48 \times 10^5 \text{ S cm}^{-3}$, which is approximately 16.3 times of that ($2.13 \times 10^4 \text{ S cm}^{-3}$) of Nafion® 117. These results indicate that the polymer electrolyte membranes fabricated in this work will be particularly promising for DMFC applications.

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1. Introduction

In recent years, polymer electrolyte membranes (PEMs) have received a lot of attention due to their application in direct methanol fuel cells (DMFCs) which are promising environmentally friendly and efficient power sources [1–3]. An ideal PEM should possess the following properties [4,5]: (i) easy synthesis from available, inexpensive raw materials; (ii) good film-forming capability and excellent mechanical property; (iii) sufficient chemical and thermal stability; (iv) low methanol diffusion and high proton conductivity. Today, sulfonated perfluoropolymers such as DuPont's Nafion® have been almost the only advanced membranes

that are used in practical DMFC systems. However, some drawbacks of sulfonated perfluoropolymers including expensive cost, high methanol diffusion/crossover, low conductivity at high temperature and low humidity as well as difficulty in synthesizing and processing have seriously hampered their widespread commercial application. Especially, the methanol diffusion from anode to cathode across the PEMs not only wastes fuel but also causes performance losses at the cathode due to the consumption of oxygen and catalyst poisoning [6–8]. Hence, the development of alternative materials overcoming these problems is strongly desired.

Recently, our group synthesized the silicon-containing sulfonated polystyrene/acrylate (Si-SPS/A) nanoparticles by emulsion polymerization method [9]. We have identified the following potential advantages for using Si-SPS/A as base polymer in comparison to Nafion®: lower membrane cost, easier and greener preparation method, better methanol barrier and higher selectivity.

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However, like other sulfonated membranes, for obtaining high proton conductivity, high sulfonation is desirable, but high sulfonation results in extreme swelling, high methanol crossover and significant loss in mechanical strength. To solve this problem and improve the properties of Si-sPS/A membrane, the Si-sPS/A, poly(vinyl alcohol) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (Si-sPS/A–PVA–PAMPS) composite membranes were prepared here through blending and crosslinking methods. The design was first based on the known excellent methanol resistance of PVA and superior ability of PAMPS to support ion conduction under low water condition [10–14], which are important considerations for direct methanol fuel cells. In addition, it is well-known that crosslinking could provide a structurally stable framework for membrane fabrication and is considered to be an effective way to restrict the extensive water swelling and methanol diffusion meanwhile enhance the mechanical property and stability of membranes [15–19]. Hence, we hoped that the crosslinked organic/inorganic Si-sPS/A–PVA–PAMPS composite membranes prepared in this work would possess good mechanical strength, excellent stability and low methanol diffusion along with the high proton conductivity.

2. Experimental section

2.1. Materials

The silicon-containing sulfonated polystyrene/acrylate (Si-sPS/A) with an ionic exchange capacity of 0.75 mmol g^{-1} was prepared via emulsion polymerization method. Detailed synthesis and characterization of polymer were reported by our previous work [9]. Poly(vinyl alcohol) (PVA) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) were used as received from Aldrich. All the other reagents and solvents were obtained commercially and used without further purification.

2.2. Membrane preparation

All the membranes were prepared by solution casting method.

The Si-sPS/A membrane was obtained by pouring the Si-sPS/A nanoparticle latex onto a clean surface of glass and drying in a vacuum oven at 60°C for 10 h and 120°C for 2 h.

The Si-sPS/A–PVA–PAMPS organic/inorganic composite membranes were prepared as follows. First, PVA was dissolved in water at 70°C with continuous stirring until a transparent solution was obtained. Then the PVA solution was cooled to room temperature and mixed with the Si-sPS/A latex. The resultant mixture was stirred continuously until homogeneous. Next, the Si-sPS/A–PVA solution was mixed with appropriate amount of PAMPS under mechanical agitation. After removing the air in a vacuum, the well-mixed solution was poured onto a glass plate and dried at 60°C for 10 h and 120°C for 2 h. The prepared membrane was soaked in a glutaraldehyde (GA)/HCl/acetone mixture solution at 40°C for 3 h. During this process, the crosslinking took place between the hydroxyl groups of PVA and the aldehyde groups of GA in the membrane due to an acid-catalyzed reaction. After chemical crosslinking reaction, the membrane was taken out, rinsed with distilled water several times to remove the nonreactive monomers. Finally, to further reduce membrane swelling and methanol diffusion, the membranes were dried and heated at 130°C for 1 h in a vacuum oven to induce physical crosslinking. The schematic process for the membrane preparation is illustrated in Fig. 1.

For convenience, the organic/inorganic composite membranes are designated as Si-sPS/A–PVA–XPAMPS, where X indicates the amount of PAMPS (wt.%) in membranes.

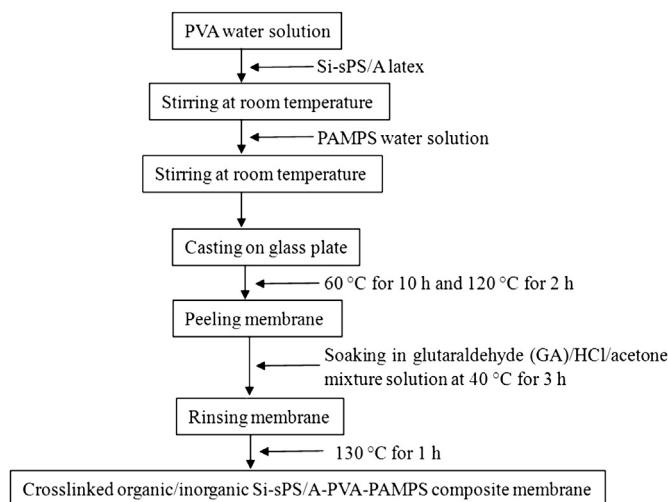


Fig. 1. The schematic preparation process for the crosslinked organic/inorganic Si-sPS/A–PVA–PAMPS composite membrane.

2.3. Membrane characterization

FTIR spectra were obtained on a Nicolet Instruments Research Series 5PC Fourier Transform Infrared Spectrometer. For all samples, KBr pellets were prepared and measured in the range from 4000 to 400 cm^{-1} .

The morphology of the membranes was investigated using a SHIMADZU SSX-550 scanning electron microscope (SEM) at an accelerating voltage of 15 kV.

The thermal stability of the Si-sPS/A and its composite membranes was investigated using a Pyris 1TGA (Perkin Elmer) thermal analyzer system. The TGA measurements were carried out under a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. Before measurement, the samples were preheated to 120°C and kept at this temperature for 20 min to remove any residual moisture. Then the samples were cooled to 100°C and reheated to 650°C .

The membrane sample was first dried at 100°C until constant weight was obtained. The dried membrane then was immersed into deionized water for 24 h at different temperatures. Subsequently, the membrane was taken out, wiped with tissue paper and quickly measured weight. The percentage of weight gain with respect to original weight was taken as the water uptake.

The methanol diffusion coefficient of membranes was determined using a glass diffusion cell as described elsewhere [20]. This cell consisted of two compartments and membrane was clamped between the two compartments. 2 M methanol was placed on one compartment and water was placed on the other one. Both closed compartments were magnetically stirred during the measurement. Prior to testing, the membranes were hydrated in distilled deionized water for at least 24 h. The increases in concentration of methanol in the water compartment with time were measured using a SHTMADU GC-8A gas chromatograph. The methanol diffusion coefficient was calculated as follows:

$$C_B(t) = \frac{A DK}{V_B L} C_A(t - t_0)$$

where A , L and V_B are the effective area, the thickness of membrane and the volume of permeate compartment, respectively. C_A and C_B are the methanol concentration in feed and in permeate compartments, respectively. DK is the methanol diffusion coefficient.

The proton conductivity of membranes was determined with AC impedance spectroscopy technique. Impedance measurements were made using SI 1260 + SI 1287 impedance analyzer over a frequency range from 10 to 10^6 Hz. Prior to measurements, the membrane was placed in distilled deionized water for at least 24 h to reach equilibrium. Then the membrane was clamped between two stainless steel electrodes and immersed into distilled deionized water to keep the relative humidity of 100% during the experiment. The proton conductivity was calculated according to the following relationship:

$$\sigma = \frac{d}{Rtw}$$

where d is the distance between the electrodes, t and w are the thickness and width of the membrane, respectively. R is the membrane resistance.

3. Results and discussion

3.1. FTIR and SEM studies

FTIR was used to identify the success of crosslinked reaction and the molecular interactions in membranes. The FTIR spectra of Si-sPS/A, Si-sPS/A-PVA and Si-sPS/A-PVA-20PAMPS membranes were measured and the results are shown in Fig. 2. It can be noted from Fig. 2 that there were multiple crosslinkings and molecular interactions in the composite membranes. First, all the membranes exhibited the characteristic peaks at 1116 cm^{-1} which was attributed to Si–O–Si asymmetric stretching vibration. The existence of the Si–O–Si peak proved the occurrence of the hydrolysis and condensation reactions of the $\text{Si}(\text{OR})_3$ groups and suggested the formation of crosslinked silica network structure in the membranes. The absorption bands at $1280\text{--}1230\text{ cm}^{-1}$ associated with the stretching vibration of C–O–C could be observed in the spectra of composite membranes, indicating that the crosslinking occurred between –OH of PVA and –CHO of GA when membrane samples were soaked in GA/HCl/acetone solution. Furthermore, in the FTIR spectrum of Si-sPS/A, the characteristic peaks at around 1034 cm^{-1} could be observed owing to the symmetric stretching vibration of

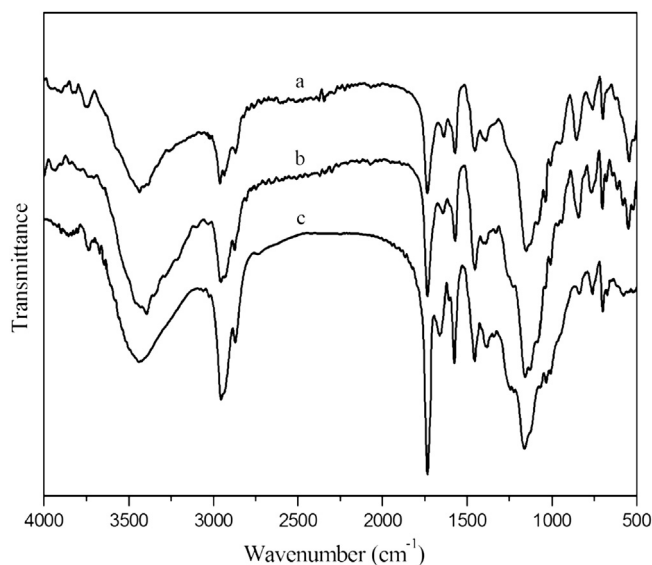
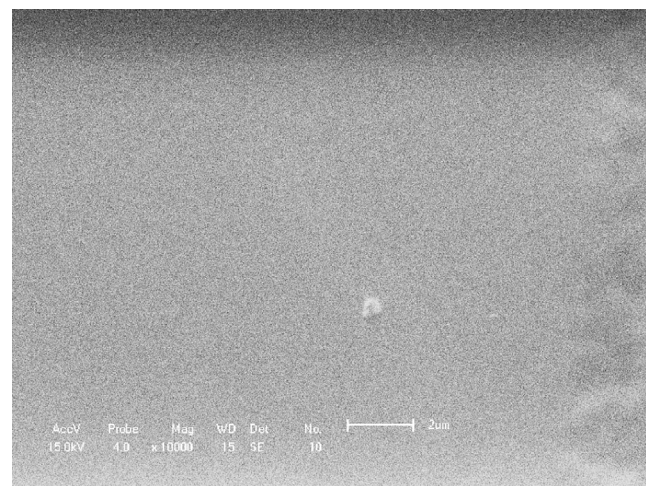
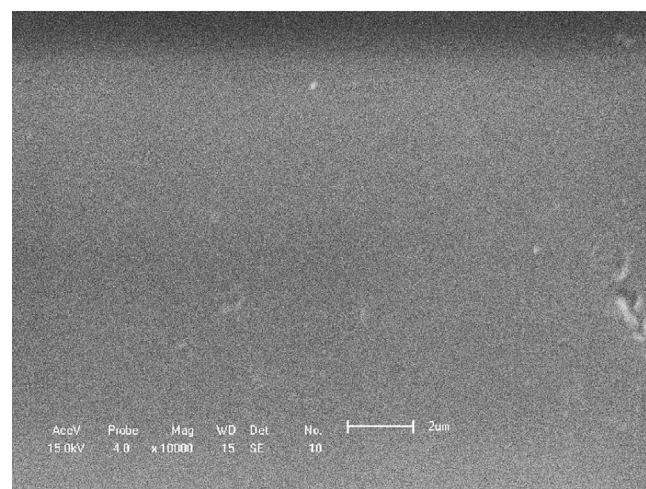


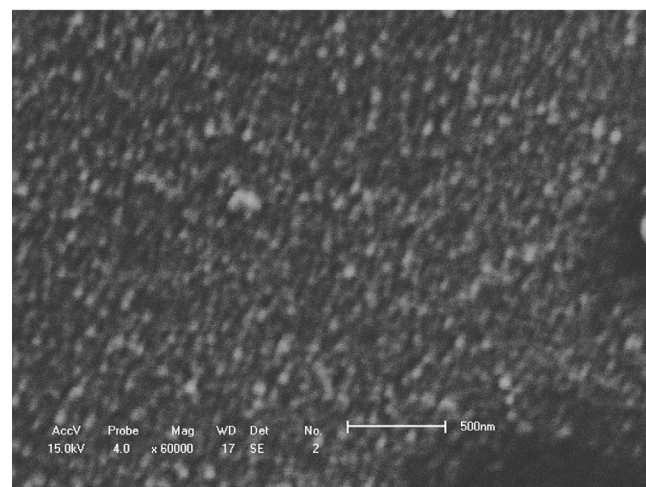
Fig. 2. FTIR spectra of (a) Si-sPS/A, (b) Si-sPS/A-PVA and (c) Si-sPS/A-PVA-20PAMPS membranes.



(a)



(b)



(c)

Fig. 3. SEM images of (a) Si-sPS/A, (b) Si-sPS/A-PVA and (c) Si-sPS/A-PVA-20PAMPS.

SO_3^- . The intensity of this peak decreased in the FTIR spectrum of Si-SPS/A–PVA, indicating that the esterized crosslinking might take place between $-\text{SO}_3\text{H}$ of Si-SPS/A and $-\text{OH}$ of PVA during thermal activated reaction. When PAMPS was added to the Si-SPS/A–PVA, the characteristic peak of SO_3^- at 1034 cm^{-1} enhanced due to the presence of SO_3H groups in PAMPS. In addition, compared with Fig. 2(a) and (b), the characteristic peak of $\text{C}=\text{O}$ at 1650 cm^{-1} and absorption band of $\text{C}=\text{C}$ at 1570 cm^{-1} in Fig. 2(c) became stronger due to the bending vibration (1650 cm^{-1}) and stretching vibration (1555 cm^{-1}) of amide groups originated from PAMPS. These increased signals demonstrated the existence of PAMPS in the final membranes. The FTIR spectra study showed that the Si-SPS/A–PVA–PAMPS organic/inorganic composite membranes with multiple crosslinked structures were fabricated successfully. Crosslinking might increase the stability of membranes and prevent the methanol crossover, which will be discussed later.

SEM was performed to study the surface morphology of the membranes. Fig. 3 shows the SEM images of Si-SPS/A, Si-SPS/A–PVA and Si-SPS/A–PVA–20PAMPS membranes. As shown in Fig. 3, no visible pores, aggregation or phase separation could be observed in SEM micrographs, indicating that PVA and AMPS were well interacted with Si-SPS and the synthesized membranes were dense.

3.2. Thermal analysis and mechanical property

The thermal degradation behavior of the Si-SPS/A and its composite membranes was studied by thermogravimetric analysis. Fig. 4 shows the TGA curves of four membranes, Si-SPS/A, Si-SPS/A–PVA, Si-SPS/A–PVA–10PAMPS and Si-SPS/A–PVA–20PAMPS. We can observe from Fig. 4 a stable Si-SPS/A at temperatures up to 200°C and there were two main weight-loss stages for Si-SPS/A. The weight losses in the first and second stages can be attributed to the decomposition of sulfonic acid groups and the destruction of the main chain and crosslinking bridge, respectively. Compared with Si-SPS/A, the thermal degradation of Si-SPS/A–PVA membrane started at a lower temperature, which could be attributed to the relative ease of PVA degradation. However, the Si-SPS/A–PVA showed higher 5% weight loss temperature due to the crosslinking. When PAMPS was incorporated into Si-SPS/A–PVA, the resulting composite membranes exhibited a decrease in thermal stability in the temperature range of $200\text{--}350^\circ\text{C}$. Additionally, TGA results

showed that the increase of PAMPS content led to the increasing weight loss at this temperature range. The possible explanation for this phenomenon is that in the Si-SPS/A–PVA–PAMPS membranes, the first weight loss (occurring between 200 and 350°C) was attributed to the degradation of OH, SO_3H and $\text{C}-\text{O}-\text{C}$. As PAMPS content increased, the amount of SO_3H increased and hence more weight loss in the first weight loss region ($200\text{--}350^\circ\text{C}$) could be observed. Fig. 4 shows that the 5% weight loss temperature for the Si-SPS/A–PVA, Si-SPS/A–PVA–10PAMPS and Si-SPS/A–PVA–20PAMPS membranes occurred at 276 , 251 and 239°C , respectively. Although the addition of PAMPS induced the membranes less stable at high temperature, the thermal stability of the composite membranes still is good enough to serve as PEMs in DMFC.

The mechanical property of composite membranes was tested by a tensile tester. The tensile strengths for the membranes with 5%, 10%, 15% and 20% PAMPS were 25.9 , 23.4 , 44.7 and 31.6 MPa , respectively, which were comparable to that of Nafion 117 (26.6 MPa). This result indicated that the composite membranes were tough enough to be used as functional proton exchange membrane materials. The elongations of the relative membranes were 12.9% , 21.4% , 9.7% and 17.3% , respectively. It could be noticed that the amount of PAMPS had no regular effect on the mechanical property. It might be because that the mechanical property of membranes may be influenced by various factors, such as the content of PAMPS, the structure, the uniformity of membranes and so on.

3.3. Water uptake behavior

The water uptake is one of essential features for polymer electrolyte membranes because it has great effects on the proton transport and stability of membranes [21]. The presence of water in the membranes is a prerequisite for achieving high proton conductivity. In general, water facilitates the proton transport and improves the fuel cells efficiency. Hence, high water absorption is expected for DMFC applications. However, when the water content exceeds its limit in the membranes, the dimensional stability, mechanical strength and methanol barrier property would be decreased, which will weak the membrane performance. Fig. 5 displays the variation of water uptake values of the composite membranes with different PAMPS content and testing

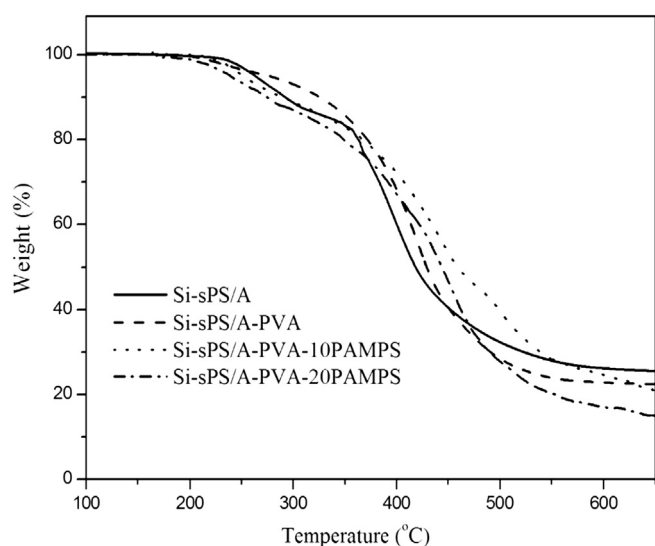


Fig. 4. TGA curves of Si-SPS/A, Si-SPS/A–PVA, Si-SPS/A–PVA–10PAMPS and Si-SPS/A–PVA–20PAMPS.

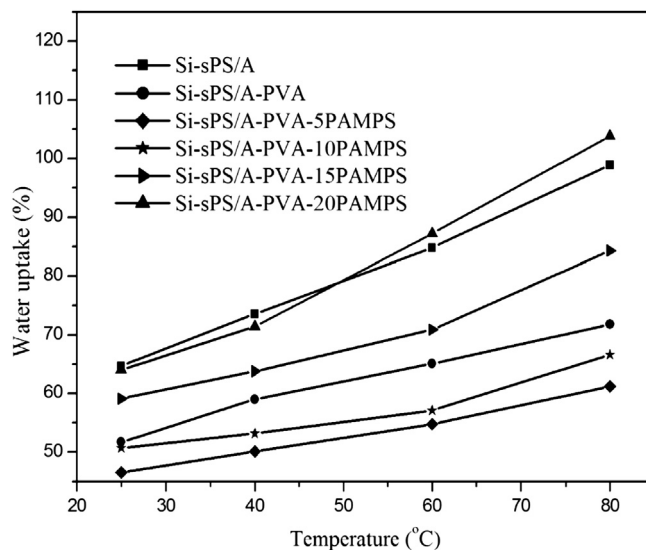


Fig. 5. Water uptakes of Si-SPS/A–PVA–PAMPS membranes with different PAMPS content and testing temperatures.

temperatures. It is noted that compared with the pure membrane, the Si-sPS/A–PVA membrane showed lower water uptake although the hydrophilic property of PVA could facilitate absorption of water. This may be explained by the fact that the extensive crosslinking achieved in the Si-sPS/A–PVA membrane led to a decrease in the chain mobility and free volume, and consequently a reduction in the vacant spaces that accommodate water molecules in the membrane. When PAMPS was added to the Si-sPS/A–PVA membrane, the water uptake values first decreased and then increased in the studied range continued up to 20% of PAMPS content as shown in Fig. 5. It is because that the introducing of PAMPS might affect the water uptake through the competition of two factors (number of hydrophilic groups and crosslinking). First, the water sorption depends on the number of hydrophilic groups in the membranes. The amount of sulfonic acid groups together with other polar groups in Si-sPS/A–PVA–PAMPS membranes increased with increasing PAMPS content, which led to the formation of larger ion clusters and hence might allow more water sorption. In addition, water uptake depends also on the crosslinking formation between the –OH groups of PVA and –SO₃H group of PAMPS. By crosslinking, more rigid and compact structure could be formed in membranes, which reduced polymer chain mobility and void space where absorbed water could be occupied, thereby resulting in a decrease in the water content. As shown in Fig. 5, the membranes containing 5% and 10% PAMPS showed lower water uptake values in comparison with the membrane without PAMPS, indicating that the effect of crosslinking was larger than that of hydrophilic groups at relatively lower PAMPS content. However, when the amount of PAMPS achieved 15% and 20%, the water uptake of composite membranes was found to be higher than that of Si-sPS/A–PVA. This behavior is mainly due to the increase of the hydrophilic groups which plays a major role in controlling the water uptake at relatively higher PAMPS content.

3.4. Methanol diffusion measurement

Table 1 gives the methanol diffusion coefficients of Si-sPS/A–PVA–PAMPS series membranes. For comparison, the methanol diffusion coefficient of Nafion® 117 measured under the same experimental conditions is also listed in Table 1. The addition of PVA was found to effectively inhibit the methanol diffusion through the Si-sPS/A membrane. The notable feature is that the diffusion coefficient of pure membrane decreased by more than a half due to the introduction of PVA and the Si-sPS/A–PVA–PAMPS membranes also showed better methanol barrier property than pure membrane. Especially, for all the membranes developed in this study, the methanol diffusion coefficients were more than one-order-of-magnitude lower than that of Nafion® 117 membrane, suggesting their potential usage in DMFCs. This may be attributed to the fuel-

blocking effect of multiple crosslinking in our membranes which had been proved by FTIR. The crosslinking not only rendered the membrane more compact, leading to more difficult permeation of the methanol molecules, but also increased the tortuosity of methanol diffusion in the permeation pathway [17]. This is definitely advantageous as it compensates for the currently sluggish anode kinetics of methanol electro-oxidation. Hence, the methanol crossover could be significantly reduced if these crosslinked organic/inorganic composite membranes are used in DMFCs.

In addition, for the Si-sPS/A–PVA–PAMPS series membranes, the methanol diffusion coefficient first decreased from 1.02×10^{-7} to $7.82 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ with PAMPS content varying from 0% to 10%, and then gradually increased to $2.47 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ when PAMPS content increased to 20% as observed from Table 1. This behavior was similar with the results observed in water uptake, indicating that methanol diffusion could occur through the hydrophilic regions. As described previously, the variation of water uptake and methanol diffusion could be affected by crosslinking and amount of sulfonic acid group. Crosslinking reduced the chain mobility and made the pathway for water and methanol molecules transporting through the membrane became narrower and fewer [22], which effectively suppressed the methanol crossover. It was found from Table 1 that the effect of crosslinking dominated the methanol transport until the amount of PAMPS reached up to 10 wt.%. The Si-sPS/A–PVA–10PAMPS membrane showed the lowest methanol diffusion coefficient ($7.82 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) which was only 1/30th of that of Nafion® 117 ($2.36 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ measured in this work). However, at higher PAMPS loading (>10 wt.%), the effect of sulfonic acid group exceeded that of crosslinking on the methanol diffusion, the membrane structure would be loosening so that the methanol could easily go through the channels formed by the large clusters. Consequently, the methanol transport through the Si-sPS/A–PVA–PAMPS membrane increased with the amount of PAMPS.

3.5. Dependence of conductivity on the PAMPS content and temperature

Proton conductivity is an important property of polymer electrolyte membranes as it directly affects the internal resistance and hence the voltage of the fuel cell [17]. Fig. 6 presents the proton conductivities of Si-sPS/A–PVA–PAMPS membranes, which are

Table 1
Property of Si-sPS/A–PVA–PAMPS membranes with the different PAMPS content.

Membranes	5% weight loss temperature (T5%)	Methanol diffusion coefficient ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$)	Selectivity ($\times 10^5 \text{ S cm}^{-3}$)
Si-sPS/A	263	4.89	0.760
Si-sPS/A–PVA	276	1.02	2.48
Si-sPS/A–PVA – 5PAMPS	–	0.799	2.72
Si-sPS/A–PVA – 10PAMPS	251	0.782	3.48
Si-sPS/A–PVA – 15PAMPS	–	0.909	3.47
Si-sPS/A–PVA – 20PAMPS	239	2.47	1.60
Nafion® 117	–	23.6	0.213

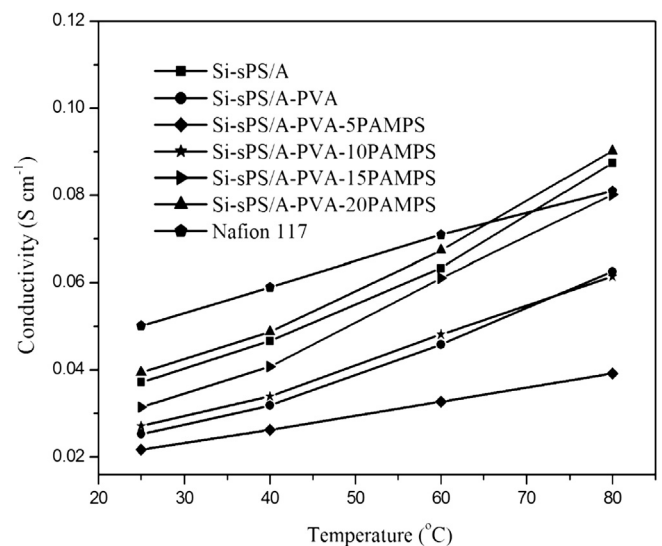


Fig. 6. Proton conductivities of Si-sPS/A–PVA–PAMPS membranes at different temperatures.

plotted as a function of temperature. We observed that the change of conductivity in Si-sPS/A–PVA–PAMPS series membranes was consistent with that of methanol diffusion coefficient with PAMPS content because the proton conductivity and the methanol diffusion take place through the same pathway [23]. It is worth noting that the proton conductivities of all the membranes were of the order of 10^{-2} S cm $^{-1}$, which was comparable to that of Nafion $^{\text{®}}$ 117. Especially, the conductivity of Si-sPS/A–PVA–20PAMPS membranes reached 9.02×10^{-2} S cm $^{-1}$ at 80 °C while Nafion $^{\text{®}}$ 117 only showed a conductivity of 8.10×10^{-2} S cm $^{-1}$ under the same measuring conditions. In addition, all the membrane samples exhibited a positive temperature-conductivity dependency as shown in Figs. 6 and 7, which suggested a thermally activated conduction process in the tested temperature range. This is because an increase in temperature can enhance the mobility of water and ions, and hence favor proton transport [24]. Furthermore, compared with Nafion $^{\text{®}}$ 117, the synthesized membranes exhibited a more pronounced increase in proton conductivity with temperature. It could be attributed to the incorporation of the inorganic phase improving water retention in the membrane due to its property of hydrophilicity [25]. Evidently, the change of conductivity with temperature followed the Arrhenius relationship in the experimental temperature range:

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{RT}$$

where R is the universal gas constant (8.314 J mol $^{-1}$ K $^{-1}$), T is the absolute temperature (K) and E_a is the activation energy of proton conduction that can be calculated from the slope of $\log \sigma$ versus $1/T$ plots. According to the Arrhenius equation, the E_a for proton conduction ranged from 9.4 to 15.2 kJ mol $^{-1}$, which was higher than that for Nafion $^{\text{®}}$ 117 membrane (7.7 kJ mol $^{-1}$). In general, the proton transport follows two mechanisms [26,27]. One is hopping mechanism (Grotthuss mechanism), wherein a proton is passed down a chain of water molecules. The protons are transferred from one solvent molecule to the next through hydrogen bonds (proton hopping). The other is vehicle mechanism, wherein a proton combines with solvent molecules by yielding a complex such as H $_3$ O $^+$ or CH $_3$ OH $_2^+$. This complex then diffuses intact. For the first mechanism, the activation energy for proton conduction was reported to be around 14–40 kJ mol $^{-1}$ [27]. From the results of the

activation energy in our system, it can be deduced that both the Grotthuss and vehicle mechanisms are responsible for the proton conduction of the composite membranes.

3.6. Selectivity

The ideal PEM for DMFC applications is expected to have high proton conductivity and low methanol diffusion. However, high proton conductivity and low methanol crossover are not commonly achieved through a single approach. Selectivity, which is defined as the ratio of proton conductivity to methanol diffusion coefficient, is a convenient measure for preliminary evaluation of PEM performance for potential DMFC application. The last column of Table 1 shows the selectivity values of Si-sPS/A–PVA–PAMPS membranes with Nafion $^{\text{®}}$ 117 as the reference. As shown in Table 1, the selectivity of composite membranes increased from 2.48×10^5 up to 3.48×10^5 S cm $^{-3}$ when the PAMPS content increased from 0 wt.% up to 10 wt.%, while the selectivity decreased to 1.60×10^5 S cm $^{-3}$ as the PAMPS increased up to 20 wt.%. Importantly, all of the membranes prepared in this study displayed higher selectivity than Nafion $^{\text{®}}$ 117. The maximum selectivity value occurred in Si-sPS/A–PVA–10PAMPS membrane was 3.48×10^5 S cm $^{-3}$ which was more than one order of magnitude greater than that of Nafion $^{\text{®}}$ 117. We can infer from these results that the Si-sPS/A–PVA–PAMPS composite membranes seem to have good potential used as PEMs in DMFCs due to their good balance between proton conductivity and methanol diffusion.

4. Conclusion

In the present work, a series of crosslinked organic/inorganic Si-sPS/A–PVA–PAMPS polymer electrolyte membranes have been successfully developed using blending and crosslinking procedures. The completion of the crosslinking and molecular interactions in membranes were confirmed by FTIR spectra. TGA analysis revealed that 5% weight loss temperature of composite membranes exceeded 239 °C, indicating their good thermal stability. The water uptake of composite membranes first decreased and then increased with the PAMPS content varying from 0 to 20% because water absorption depended not only on the amount of hydrophilic groups, but also on the crosslinking. The conductivity values of the composite membranes were of the order of 10^{-2} S cm $^{-1}$, which was comparable to commercially available Nafion $^{\text{®}}$ 117. More importantly, the obtained membranes revealed an effective methanol barrier due to their unique structural features, and the methanol diffusion coefficient values of all composite membranes were much lower than that of Nafion $^{\text{®}}$ 117 membrane. The membranes containing 10 wt.% of PAMPS showed the lowest methanol diffusion coefficient (7.82×10^{-8} cm 2 s $^{-1}$) which was only 1/30th of that of Nafion $^{\text{®}}$ 117. Furthermore, it should be mentioned that the membranes developed in this work exhibited much higher selectivity values than that of Nafion $^{\text{®}}$ 117. Considering the good thermal stability, excellent methanol barrier and high selectivity, the crosslinked organic/inorganic composite membranes, especially Si-sPS/A–PVA–10PAMPS membrane, might be potential candidates as polymer electrolyte membranes for DMFC application.

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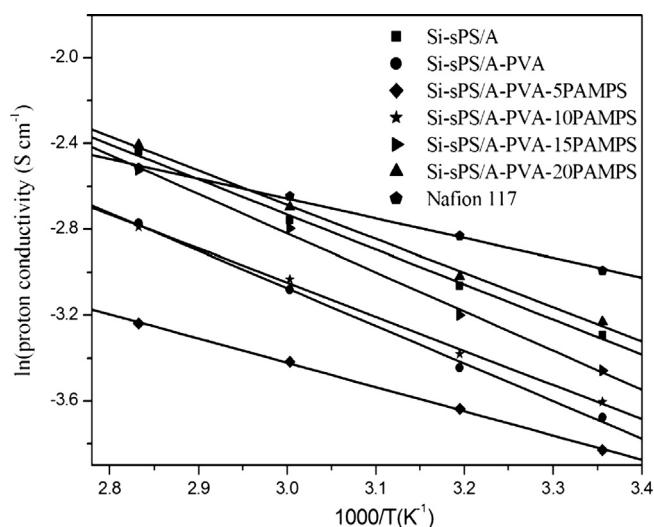


Fig. 7. Temperature dependences of the proton conductivity for Si-sPS/A–PVA–PAMPS membranes.

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